

What is claimed is:

1. A method for the preparation of glycoconjugates comprising reacting under condensing conditions involving acid or metal catalysis at least two saccharides selected from the group consisting of:

- A. aldomonosaccharides
- B. deoxyhexoses
- C. N-acetyldoses
- 10 D. sialic acids
- E. hexuronic acids
- F. oligosaccharides containing a saccharide from any one of groups A – E
- G. polysaccharides containing a saccharide from any one of groups A – E

- 15 so that said saccharides are selected from at least two of groups A – G;

in order to form a glycosidic bond between said saccharides through any free hydroxyl group position in said saccharides.

- 20 2. The method according to claim 1, wherein group A consists of pentoses and hexoses.

3. The method according to claim 1, wherein group B consists of fucose and rhamnose.

- 25 4. The method according to claim 2, wherein group A consists of ribose, xylose and arabinose.

5. The method according to claim 1, wherein group C consists of N-acetylglucosamine and N-acetylgalactosamine.

- 30 6. The method according to claim 1, wherein group D consists of N-acetyl neuraminic acid.

7. The method according to claim 1, wherein group E consists of galactouronic acid and glucuronic acid.

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8. The method according to claim 1, wherein group F consists of lactose, maltose, maltooligosaccharides, isomaltose, isomaltooligosaccharides, sucrose, fucose

oligosaccharides, xylooligosaccharides, mannose oligosaccharides, GlcNAc oligosaccharides, GalNAc oligosaccharides and cyclic oligosaccharides.

9. The method according to any one of claims 1 - 8, wherein said saccharides are non-protected reducing monosaccharides or oligosaccharides.
10. The method according to claim 1, wherein said condensing conditions involve acid or metal catalysis.
11. The method according to claim 10, wherein the acid catalysing the reaction is hydrochloric acid, sulphuric acid, organic acid, phosphoric acid or mixtures thereof.
12. The method according to claim 10, wherein the acid catalysing the reaction is not hydrogen fluoride.
13. The method according to claim 1, wherein said saccharides are in solid or semisolid state.
14. The method according to claim 1, wherein the reaction is conducted at a temperature under 180 degrees of Celsius, preferably 140 – 180 degrees of Celsius.
15. The method according to claim 14, wherein the reaction is conducted at a temperature of from 45 to 85 degrees of Celsius.
16. The method according to claim 14, wherein the reaction is conducted at a room temperature.
17. The method according to claim 1, wherein the reaction further comprises an alcohol, preferably a polyol.
18. The method according to claim 17, wherein the reaction comprises an excess of polyol.
19. The method according to the claim 1, wherein the method further comprises a step of reacting a glycoconjugate formed under condensing conditions with an excess of polyol.
20. The method according to any one of claims 17 - 19, wherein two mono- or oligosaccharides of the saccharide or glycoconjugate are linked to a single polyol molecule.

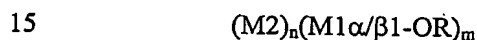
21. The method according to claim 1, wherein at least one of said saccharides have been reacted with a polyol before subjecting said saccharide to the method of claim 1.
22. The method according to the claim 1, wherein the chain length of reaction products
5 obtained is two to ten monosaccharide residues.
23. The method according to the claim 1, wherein the method further comprises a step of isolating specific reaction products.
- 10 24. The method according to the claim 1, wherein the method further comprises a step of derivatizing the reducing end of reaction products.
25. The method according to claim 24, wherein the final products of the method are derivatized polydextroses.
- 15 26. The method according to the claim 24, wherein the reducing end derivatization groups include aglycons selected from the group consisting of: lipids, spacers, solid phases, cross-linking chemicals and biotin.
- 20 27. The method according to claim 1, wherein the reaction products contain random mixtures of linkages with no specific preference for 1-6-linkages.
28. The method according to claim 1, wherein at least one of the saccharides are selected from group F or G.
- 25 29. The method according to claim 28, wherein the linkage structure of the saccharide of group F or G remains intact in the reaction.
- 30 30. The method according to claim 1, wherein the reaction products do not contain or contain minimum amounts of anhydro products.
31. The method according to claim 30, wherein the anhydro product is levoglucosan.
32. The method according to claim 1, wherein the reaction products form an
35 oligosaccharide library.
33. An oligosaccharide library obtained by a method according to claim 32 optionally having an essentially same mass spectrum of any of the Figures 1-13.

34. Use of the oligosaccharide library according to claim 33 for screening of biologically active oligosaccharides.
35. A neoglycolipid composition comprising a non-natural oligosaccharide mixture comprising randomly linked oligomers of monosaccharides from at least two of groups A-E as defined in claim 1, when said oligomers are linked to a hydrophobic aglycon.
36. A neoglycolipid composition according to claim 35, wherein the non-natural oligosaccharide comprises single type of monosaccharides or oligosaccharides.
37. A neoglycolipid composition according to claim 35, wherein said composition is obtained by the method according to claim 1 or said composition comprises oligosaccharide fractions obtained by the method according to claim 1.
38. The method according to claim 1, wherein the products of the reaction comprise a mixture or library of oligosaccharides or polysaccharides including carbohydrates comprising different substrate carbohydrates glycosidically linked to each other and/or, when substrate carbohydrate(s) is/are oligosaccharide(s) or polysaccharide(s), monosaccharide residues from the different substrates glycosidically linked to each other.
39. The method according to claim 1, wherein the products of the reaction comprise a mixture or library of oligosaccharides or polysaccharides including carbohydrates comprising monosaccharide residues from all different substrates and said monosaccharide residues are glycosidically linked to each other.
40. The method according to claim 1, wherein products of the reaction comprise a mixture or library of oligosaccharides or polysaccharides including carbohydrates comprising: different substrate carbohydrates glycosidically linked to each other and/or, when substrate carbohydrate(s) is/are oligosaccharide(s) or polysaccharide(s), monosaccharide residues from the different substrates glycosidically linked to each other and/or homotypic glycosidically linked oligomer or polymers of one or several of the substrate carbohydrates and/or glycosidically linked oligomers or polymers of the monosaccharides from the substrate.
41. The method according to claim 1, wherein products of the reaction comprise a mixture or library of oligosaccharides or polysaccharides including carbohydrates comprising different substrate carbohydrates glycosidically linked to each other

and/or, when substrate carbohydrate(s) is/are oligosaccharide(s) or polysaccharide(s), monosaccharide residues from the different substrates glycosidically linked to each other and/or homotypic glycosidically linked oligomer or polymers of all of the substrate carbohydrates and/or glycosidically linked homotypic oligomers or polymers of the monosaccharides from all of the substrate carbohydrates.

42. The method according to claim 1, wherein the products of the reaction comprise a mixture or library of oligosaccharides or polysaccharides including carbohydrates comprising mixed monosaccharide residues from the different substrates glycosidically linked to each other and glycosidically linked homotypic oligomers or polymers of the monosaccharides from the substrate carbohydrates.

43. An oligosaccharide library or mixture comprising saccharides according to formula



wherein n is an integer from 1 to 4, and integer m is either 0 or 1 and M1 monosaccharide units are selected from the groups A, B, D as defined in claim 1 and M2 is selected from groups A-E as defined in claim 1; OR is is a methyl glycoside or ethyl glycoside.

44. The oligosaccharide library or mixture according to claim 43, wherein the oligosaccharide mixture is defined by a mass spectrum and at least four different structures comprising unit M2 can be observed by NMR spectrometry.

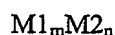
45. The method according to any one of claims 1, 28 or 29 wherein the oligosaccharide or polysaccharide is reacted with a monosaccharide selected from groups A-E.

46. The method according to claim 1, wherein a polysaccharide is reacted with a monosaccharide.

47. The method according to the claim 1, wherein two polysaccharides are reacted with each other.

48. The method according to claim 32, wherein the polysaccharides comprise different monosaccharide residues, preferably from different groups A-E.

49. The method according to any of claims 30-33, wherein the polysaccharide is selected from the group of polysaccharides comprising glucose, galactose, mannose, xylose, fucose, N-acetylglucosamine, N-acetylgalactosamine, or sialic acid.
- 5 50. The method according to claim 1, wherein the reaction mixture also comprises methyl alcohol and oligosaccharides formed are methyl glycosides.
51. The method according to claim 1, wherein the reaction products are further derivatized.
- 10 52. The method according to claim 1, wherein the monosaccharide is selected selected from the group Fuc, Ara, GalA and sialic acid.
53. The method according to claim 45, wherein said polysaccharide is starch.
- 15 54. Use of the reaction products obtained by a method of claim 1 or compositions containing the products as mass finger prints to mark food, beverage or other products.
55. An oligosaccharide mixture or fraction comprising oligosaccharides according to the Formula 1:
- 20



- wherein monosaccharide units M1 and M2 selected from at least two of groups A-E as defined in claim 1, are glycosidically linked in any order and m and n are varying integers
- 25 for different oligosaccharide components from 0 to 6 with the provision that the isomers are present in the mixture so that each oligosaccharide has at least two possible isomerically linked forms between every linkage between monosaccharide residues.

56. An oligosaccharide mixture or fraction comprising oligosaccharides according to Formula 2:
- 30



- wherein M1 and M2 and M3 are monosaccharide units from at least two of groups A-E as defined in claim 1 with the provision that M1, M2 and M3 are glycosidically linked to each other in any order in linear or branched sequence and m and n and o are varying integers
- 35 for different oligosaccharide components from 0 to 6, and with the provision that the

isomers are present in the mixture so that each oligosaccharide has at least two possible isomerically linked forms between every linkage between monosaccharide residues.

57. An oligosaccharide mixture or fraction comprising oligosaccharides according to the
5 Formula 3:



- 10 wherein M1, M2, M3, and M4 are monosaccharide units from at least two of groups A-E as defined in claim 1 with the provision that M1, M2, M3, and M4 are glycosidically linked to each other in any order in linear or branched sequence and m, n, o, and p are varying integers for different oligosaccharide components from 0 to 6 with the provision that the isomers are present in the mixture so that each oligosaccharide has at least two possible isomerically linked forms between every linkage between monosaccharide
15 residues.

58. The oligosaccharide mixture or fraction according to any one of claims 55-57, wherein the oligosaccharide mixture has a mass spectrum corresponding to the Formula 1, 2 or 3.

- 20 59. The oligosaccharide mixture or fraction according to claim 58, wherein an NMR spectrum of the fraction or mixture indicates presence of at least two different linkage forms for every monosaccharide residue species in the mixture.

- 25 60. A method for the preparation of glycoconjugates comprising reacting under condensing conditions a reducing non-protected monosaccharide with a partially protected monosaccharide.

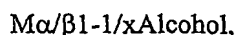
- 30 61. The method according to claim 60, wherein the secondary hydroxyl groups of the partially protected monosaccharide are protected, and the primary hydroxyl group and anomeric hydroxyl group of the partially protected monosaccharide are non-protected.

62. The method according to claim 60, wherein the primary hydroxyl group and anomeric hydroxyl group of the partially protected monosaccharide are protected.

- 35 63. The method according to claim 60, wherein the primary hydroxyl group of the partially protected monosaccharide residue is protected.

64. The method according to claim 60, wherein all non-anomeric hydroxyl groups of the partially protected monosaccharide are protected and the anomeric hydroxyl group of the partially protected monosaccharide is non-protected.
- 5 65. The method according to claim 60, wherein the anomeric hydroxyl group of the partially protected monosaccharide is protected.
66. The method according to claim 60, wherein said partially protected monosaccharide is alkyl glycoside with no other protecting groups.
- 10 67. The method according to claim 66, wherein said alkyl glycoside is a methyl glycoside alcohol glycoside or ethylglycoside.
68. The method according to claim 60 comprising a further step of isolating products
15 according to the Formula
- $$(M2)_n(M1\alpha/\beta1-OR)_m$$
- wherein n is an integer, for oligosaccharides n is 1 to 10 and for polysaccharides $n > 10$,
20 integer m is either 0 or 1, and M1 and M2 are monosaccharide units selected from the groups A-E as defined in claim 1; OR is an ether glycosidically linked to M1, preferably OR is a methyl ether.
69. A method for the preparation of self-condensed glycoconjugates comprising
25 polymerising under condensing conditions an at least partially protected saccharide with at least one hydroxyl group which is protected by an acid labile leaving group and an activating group at anomeric position, wherein the saccharide is polymerised by reacting the anomeric position with the O-atom protected by the leaving group.
- 30 70. The method according to claim 69, wherein said leaving group is a silyl ether and said activating group is a common saccharide activating group.
71. The method according to claim 69, wherein the reaction is catalysed by Lewis acid.
- 35 72. The method according to claim 71, wherein scandium is used as a Lewis acid catalyte.
73. The method according to claim 69, wherein said activating group is a halogenide.

74. The method according to claim 69, wherein one hydroxyl group of the saccharide is protected with an acid labile leaving group and other non-anomeric hydroxyl groups of the saccharide are stably protected.
- 5 75. The method according to claim 69, wherein the leaving group is a silyl group.
76. An oligomeric lactoside substance comprising at least 2 lactosyl residues linked glycosidically together.
- 10 77. A dimeric lactoside wherein glucose residues are 1-1-linked to each other.
78. A method for the preparation of self-condensed glycoconjugates comprising polymerising under condensing conditions an anomERICALLY activated carbohydrate, wherein the hydroxyl groups of the carbohydrate are not protected and wherein the
- 15 activated carboxyl group is reacted with any free hydroxyl group of the carbohydrate to form a polymer or an oligomer.
79. The method according to claim 78, wherein a Lewis acid or the Lewis acid scandium is used as catalyst.
- 20 80. The method according to claim 78, wherein the carbohydrate is lactose or comprises lactosyl structure at the reducing end.
81. A method for the preparation of glycoconjugates comprising reacting under condensing
- 25 conditions one type of non-protected monosaccharides selected from the group consisting of Glc, Gal, Man, Xyl, Ara, Fuc, Rha, GlcNAc, ManNAc, GalNAc, GlcA, GalA and sialic acid to produce an oligosaccharide mixture.
82. The method according to claim 81, wherein the monosaccharide is selected from the
- 30 group consisting of Fuc, Ara, GalA and sialic acid.
83. The method according to claim 81 further comprising a step of isolating oligosaccharides from the reaction mixture, wherein an oligosaccharide mixture comprising 2-4 monosaccharide residues is isolated.
- 35 84. An essentially pure monosaccharide conjugate mixture consisting of all non-reducing monosaccharide conjugates according to the formula



wherein M is a monosaccharide residue selected from the group consisting of Glc, Gal, Man, Xyl, Fuc, GlcNAc with the provision that M is α - or β -linked to position 1 or another hydroxyl marked by x of a polyalcohol substance preferably xylitol, sorbitol, galactitol, or mannitol, when the conjugate mixture optionally comprises also the polyalcohol in free form.

85. A method to produce essentially pure composition according to claim 84, comprising reacting the saccharide mixture as defined in claim 1 under condensing conditions and using an excess of polyalcohol and optionally isolating the monosaccharide conjugate from the polyalcohol excess after the reaction.

86. A method for the preparation of glycoconjugates comprising reacting under condensing conditions a polysaccharide with polyalcohol.

87. The method according to claim 86, wherein said polysaccharide is starch.

88. A method of production of a tagged carbohydrate product comprising the steps of:

- a) tagging at least one carbohydrate substrate with a tag molecule;
- b) reacting at least one tagged carbohydrate substrate with at least one non-tagged or differentially tagged carbohydrate substrate;
- c) contacting tagged reaction products with immobilised matrix having affinity for the tag molecule(s).

89. The method according to claim 88, wherein the carbohydrate substrate to be tagged is tagged to the reducing end.

90. The method according to 88, wherein the carbohydrate substrate is tagged to an amine group.

91. The method according to claim 88, 89, or 90, wherein the carbohydrate substrate is tagged with a tag molecule having an aminoxy group linked to the tag structure.

92. The method according to any one of claims 88-91, wherein said tag molecule comprises biotin or a carboxylic acid group.

93. The method according to any one of claims 88-92, wherein all substrates are tagged.